

CATALYSTS USED FOR OLEFINE POLYMERIZATION AND THE PREPARATION THEREOF

Field of the Invention

The present invention relates to a catalyst used for olefine polymerization and the preparation thereof. The present invention also relates to a method of polymerizing olefines by using the catalyst of the present invention.

Background of the Invention

Polyolefine is a very important category of polymeric materials. Half of the plastics are polyolefine. They are widely used in industry, agriculture, national defense, communication, transportation and human daily life. Olefines can be polymerized to form macromolecular compounds called polyolefines by using a catalyst. Therefore, catalyst is a key to the development of polyolefine industry which plays a very important role in controlling the structures and properties of polyolefines.

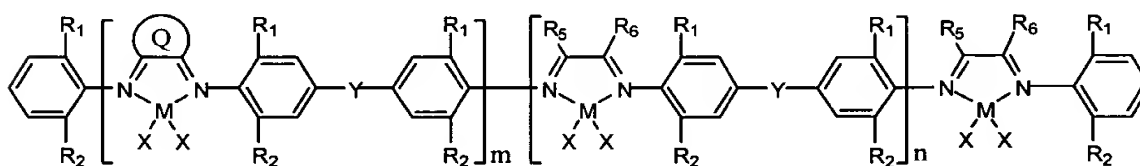
Although the conventional Ziegler-Natta catalysts are still widely used in the industrial production of polyolefines, they are not good catalysts for the manufacture of linear low-density polyethylenes (LLDPE). Recently, it was found that zirconocene, a representative of the metallocene catalysts, possesses very high catalytic activity to copolymerize olefines and can be used for the production of LLDPE. However, an α -olefine (such as butene-1, hexene-1, octene-1, and the like) as the second monomer is required by using metallocene to catalyze the polymerization of olefine for the production of LLDPE, which complicated the process of polymerization. In 1996, Johnson in Du Pont Co. disclosed that α -diimino nickel(II) could be used as an olefine polymerization catalyst (WO 96/23010). With the action of a co-catalyst of methyl aluminoxane (MAO) or modified methyl aluminoxane (MMAO), it is possible to homopolymerize ethylene. By controlling the polymerization conditions, it is possible to obtain polyethylene (PE)

including LLDPE with high molecular weight, low density and desired degree of branching.

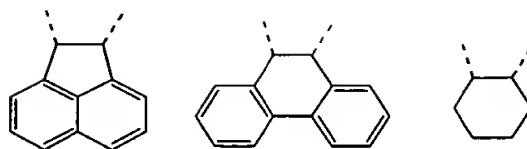
Disclosure of the Invention

It is an object of the present invention to provide a catalyst used for olefine polymerization which is a polynuclear α -diimino Ni(II). The precursor of this catalyst is a polynuclear α -diimino Ni(II) complex. The polynuclear α -diimine Ni(II) complex can be activated by a neutral Lewis acids such as MAO, MMAO, which then catalyze the polymerization of ethylene into high molecular weight branched polymeric materials.

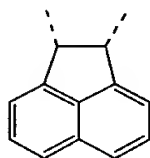
The polynuclear α -diimino Ni(II) complex of the present invention has the following structure:



wherein M is Ni; X is Cl or Br, and preferably X is Br; m and n is dependently an integer from 0 to 100, and preferably m is from 1 to 20 and n is from 0 to 30 or m is from 0 to 20 and n is from 1 to 30, more preferably m is from 1 to 10 and n is from 0 to 20 or m is from 0 to 10 and n is from 1 to 20; R₁ and R₂ may be same or different, and is dependently H, methyl, ethyl, isopropyl or tert-butyl, preferably R₁ is isopropyl and R₂ is methyl or isopropyl; Y is CR₃R₄, wherein R₃ and R₄ may be same or different, and is dependently H, methyl, ethyl, propyl, butyl or phenyl, preferably R₃ and R₄ are the same, and are H or methyl, or R₃ and R₄ forming a cyclohexyl group; R₅ and R₆ may be same or different, and is dependently methyl, ethyl or heterocyclic group (such as 2-pyridyl group), preferably R₅ and R₆ are the same, and are methyl; Q is a divalent residual represent by the following formula or a mixture thereof:

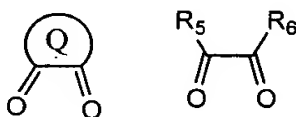


preferably Q is a divalent residual of the following formula:



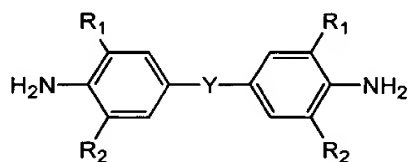
The polynuclear α -diimino Ni(II) complex of the present invention can be prepared by a method comprising the following steps:

(a) condensing an α -diketone represented by the formula or a mixture thereof,



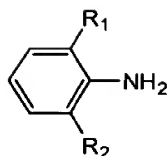
wherein, Q, R_5 and R_6 are as defined above,

a substituted aromatic diamine represented by the formula



wherein, R_1 , R_2 and Y are as defined above,

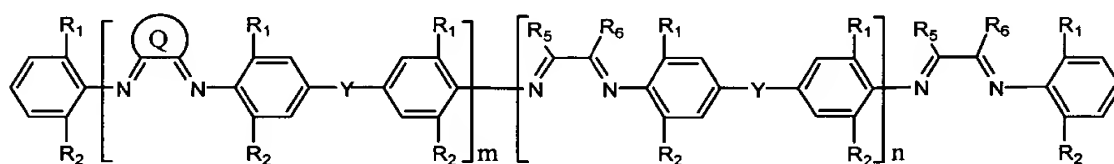
and a substituted aromatic amine represented by the formula



wherein, R_1 and R_2 are as defined above,

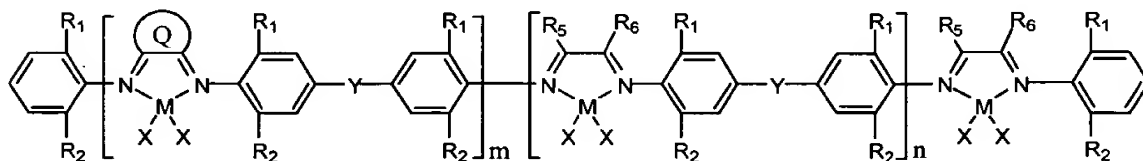
in a medium of alcohol, aromatic hydrocarbon, alcohol-ether mixture, or alcohol-halogenated hydrocarbon mixture and under the catalytic action of HCOOH , CF_3COOH or HX , wherein X is F , Cl , Br , or I ;

thereby obtaining an oligomer of substituted α -diimine of the formula



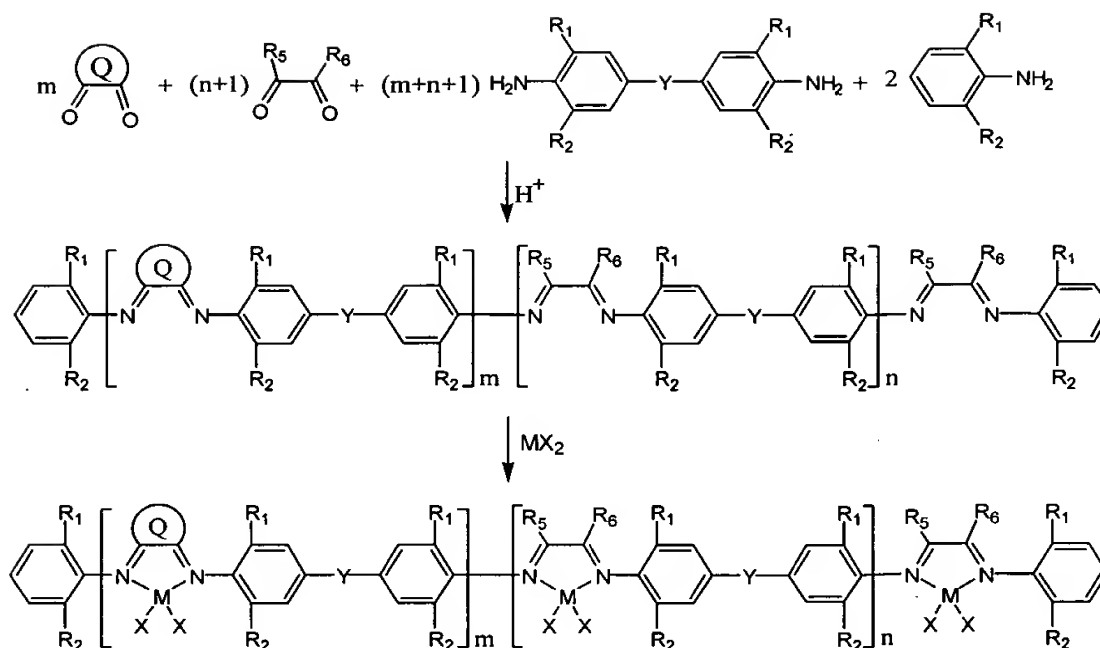
wherein, R_1 , R_2 , R_5 , R_6 , Q , Y , m and n have the same definition of above;

(b) carrying out coordination reaction of the oligomer of step (a) with NiX_2 , wherein X is Cl or Br , in the absence of water and oxygen, thereby obtaining a polynuclear α -diimino Ni(II) complex of the following formula:



wherein, R_1 , R_2 , R_5 , R_6 , Q , Y , M , X , m and n have the same definition of above.

The reaction process can be represent by the following scheme:



wherein, $R_1, R_2, R_5, R_6, Q, Y, M, X, m$ and n have the same definition of above.

The polynuclear α -diimino Ni(II) complex of the present invention is capable of catalyzing the polymerization of ethylene under the action of neutral Lewis acid such as MAO or MMAO and the like. Thus, polyethylene with high molecular weight can be obtained.

Examples

Example 1

To a 150 ml reaction flask, 1.457 g (8.0 mmol) of acenaphthenedione, 1.405 g (4.0 mmol) of di(4-amino-3-chloro-5-isopropylphenyl)methane, and 50 ml ethanol were added, stirred and dissolved. Then, 1.0 ml HCOOH was added dropwise and the mixture was refluxed for 24 hours. After cooling, 1.507 g (8.5 mmol) of 2,6-diisopropyl aniline was added and the mixture was heated, refluxed for 24 hours. After cooling, the mixture was poured into 200 ml of petroleum ether under stirring and filtered. The filter cake was washed twice with cold methanol and dried in vacuum at $60^\circ C$ for 48 hours. 3.37 g of dimer of α -diimine (yield 84.4%) was obtained.

Example 2

To a 150 ml reaction flask, 1.093 g (6.0 mmol) of acenaphthenedione, 1.579 g (4.0 mmol) of 2,2-di(4-amino-3,5-diisopropyl phenyl) propane, and 50 ml ethanol were added, stirred and dissolved. Then 1.0 ml trifluoroacetic acid was added dropwise and the mixture was refluxed for 24 hours. After cooling, 0.762g (4.3 mmol) of 2,6-diisopropyl aniline was added. The following procedure was the same as Example 1. 2.78 g of trimer of α -diimine (yield 87.9%) was obtained.

Example 3

To a 150 ml reaction flask, 1.093 g (6.0 mmol) of acenaphthenedione, 2.055 g (4.5 mmol) of 1,1'-di(4-amino-3,5-diisopropylphenyl) phenylethane, and 50 ml toluene were added, stirred and dissolved. Then three drops of HCl were added, and the mixture was refluxed for 8 hours. After cooling, 0.585 g (3.3 mmol) of 2,6-diisopropyl aniline was added and the mixture was heated, and refluxed for 12 hours. After cooling and placing overnight, the reactant was filtered. The filter cake was washed twice with cold methanol and dried in vacuum at 60°C for 48 hours. 3.17 g of oligomer of α -diimine (yield 91.5%) was obtained.

Example 4

To a 150 ml dried reaction flask, 1.366 g (7.5 mmol) of acenaphthenedione, 2.115g (6.0 mmol) of 2,2-di(4-amino-3-methyl-5-isopropylphenyl) butane, and 50 ml ethanol were added, stirred and dissolved. 1.0 ml of HCOOH was added dropwise, and the mixture was refluxed for 24 hours. After cooling, 0.478 g (3.2 mmol) of 2-methyl-6-isopropyl aniline was added, and the mixture was heated and refluxed for 24 hours. The rest of the procedure was the same as in Example 1. 3.38 g of oligomer of α -diimine (yield 92.3%) was obtained.

Example 5

To a 150 ml dried reaction flask, 1.275 g (7.0 mmol) of acenaphthenedione, 2.608 g (6.0 mmol) of 1,1-di(4-amino-3,5-diisopropylphenyl) cyclohexane, and 50 ml ethanol

were added, stirred and dissolved. Then, 1.0 ml HCOOH was added and the mixture was refluxed for 24 hours. After cooling, 0.390 g (2.2 mmol) of 2,6-diisopropyl aniline and 10 ml chloroform was added, and the mixture was heated and refluxed for 24 hours. The rest of the procedure was the same as in Example 1. 3.67 g of oligomer of α -diimine (yield 92.1 %) was obtained.

Example 6

To a 150 ml dried reaction flask, 0.984 g (5.4 mmol) of acenaphthenedione, 0.186 g (0.6 mmol) of di(4-amino-3,5-diethylphenyl) methane, 1.826 g (4.2 mmol) of 1,1-di(4-amino-3,5-diisopropylphenyl) cyclohexane, and 40 ml ethanol were added, stirred and dissolved. Then 1.0 ml HCOOH was added dropwise and the mixture was refluxed for 24 hours. After cooling, 0.248 g (1.4 mmol) of 2,6-diisopropyl aniline and 10 ml tetrahydrofuran were added, and the mixture was heated and refluxed for 24 hours. The rest of the procedure was the same as in Example 1. 3.07 g of oligomer of α -diimine (yield 93.7 %) was obtained.

Example 7

The process of Example 6 was carried out, except that 0.169 g (0.6 mmol) of 2,2-di(4-amino-3,5-dimethylphenyl) propane was used in place of Di(4-amino-3,5-diethylphenyl) methane in Example 6. 3.02 g of dimer of α -diimine (yield 92.7%) was obtained.

Example 8

The process of Example 6 was carried out, except that 0.186 g (0.6 mmol) of di(4-amino-3-tert-butylphenyl)methane was used in place of Di(4-amino-3,5-diethylphenyl) methane in Example 6. 3.00 g of dimer of α -diimine (yield 91.6%) was obtained.

Example 9

To a 150 ml reaction flask, 1.664 g (8.0 mmol) of phenanthrenequinone, 1.354 g (4.0 mmol) of 2,2-di(4-amino-3-methyl-5-isopropylphenyl)propane, and 50 ml ethanol were added, stirred and dissolved. Then, 1.0 ml trifluoroacetic acid was added dropwise

and the mixture was refluxed for 3 days. After cooling, 1.269 g (8.5 mmol) of 2-methyl-6-isopropyl aniline was added, and the mixture was heated and refluxed for 24 hours. After cooling and placing overnight, the reactant was filtered. The filter cake was washed twice with cold methanol and vacuum dried at 60°C for 48 hours. 3.36 g of oligomer of α -diimine (yield 85.6%) was obtained.

Example 10

To a 150 ml reaction flask, 0.897g (8.0 mmol) of 1,2-cyclohexanedione, 1.466 g (4.0 mmol) of di(4-amino-3,5-diisopropyl phenyl)methane, and 50 ml ethanol were added, stirred and dissolved. Then 1.0 ml of formic acid was added dropwise and the mixture was refluxed for 5 days. After cooling, 1.596 g (9.0 mmol) of 3,5-diisopropyl aniline was added, and the mixture was heated and refluxed for 7 days. After cooling, the mixture was concentrated and eluted by column (petroleum ether/ethyl acetate mixed solvent as eluant). 1.72 g of product was obtained (yield 49.2%).

Example 11

To a 150 ml reaction flask, 1.698 g (8.0 mmol) of 2,2'-di-pyridyl ethanedione, 1.466 g (4.0 mmol) of di(4-amino-3,5-diisopropylphenyl) methane, 50 ml of toluene and 3 drops of HCl were added, and the mixture was refluxed for 4 days. After cooling, 1.773 g (10.0 mmol) of 3,5-diisopropyl aniline was added and the mixture was heated and refluxed for 7 days. Then the mixture were cooled, concentrated and eluted by column (petroleum ether/ethyl acetate mixed solvent as eluant), and 1.49 g of product was obtained (yield 34.8%).

Example 12

To a 150 ml reaction flask, 0.620 g (7.2 mmol) of 2,3-butanedione, 2.346 g (6.4 mmol) of di(4-amino-3,5-diisopropyl phenyl) methane, and 50 ml of ethanol were added and stirred. Then, 1.0 ml of formic acid was added dropwise, and the mixture was heated and refluxed for 24 hours. After cooling, 0.319 g (1.8 mmol) of 2,6-diisopropyl aniline was added and the mixture was heated and refluxed for 24 hours. After cooling, The mixture was poured into 200 ml petroleum ether while stirring and then filtered. The filter cake was

washed twice with methanol and vacuum dried at 60°C for 48 hours. 2.68 g of oligomer of α -diimine (yield 89.3%) was obtained.

Example 13

To a 150 ml reaction flask, 0.560 g (6.5mmol) of 2,3-butanedione, 2.199 g (6.0 mmol) of di(4-amino-3,5-diisopropyl phenyl) methane, and 50 ml of ethanol were added and stirred. Then, 1.0 ml of formic acid was added dropwise, and the mixture was heated and refluxed for 24 hours. After cooling, 0.212 g (1.2 mmol) of 2,6-diisopropyl aniline was added. The rest of the procedure was the same as in Example 12. 2.51 g of oligomer of α -diimine (yield 92.9%) was obtained.

Example 14

To a 150 ml reaction flask, 0.585 g (6.8 mmol) of 2,3-butanedione, 2.346 g (6.4 mmol) of di(4-amino-3,5-diisopropylphenyl) methane, and 50 ml of ethanol were added and stirred. Then, 1.0 of ml formic acid was added dropwise, and the mixture was heated and refluxed for 24 hours. After cooling, 0.177 g (1.0 mmol) of 2,6-diisopropyl aniline was added. The rest of the procedure was the same as in Example 12. 2.69 g of oligomer of α -diimine (yield 95.1%) was obtained.

Example 15

To a 150 ml reaction flask, 0.631 g (6.3 mmol) of 2,3-butanedione, 2.200 g (6.0 mmol) of di(4-amino-3,5-diisopropylphenyl) methane, and 50 ml of ethanol were added and stirred. Then, 1.0 ml formic acid was added dropwise, and the mixture was heated and refluxed for 24 hours. After cooling, 0.142 g (0.8mmol) of 2,6-diisopropyl aniline was added. The rest of the procedure was the same as in Example 12. 2.60 g of oligomer of α -diimine (yield 96.0%) was obtained.

Example 16

To a dried 150 ml reaction flask, 1.093 g (6.0 mmol) of acenaphthanedione, 0.312g (1.5 mmol) of phenanthrenequinone, 2.368 g (6.0 mmol) of 2,2-di(4-amino-3,5-diisopropylphenyl)propane, and 50 ml of ethanol were added, stirred and dissolved. Then,

1.0 ml of formic acid was added dropwise, and the mixture was heated and refluxed for 24 hours. After cooling, 0.567 g (3.2mmol) of 2,6-diisopropyl aniline was added, and the mixture was heated and refluxed for 24 hours. The rest of the procedure was the same as in Example 1. 3.78g of oligomer of α -diimine (yield 93.7%) was obtained.

Example 17

To a dried 150 ml reaction flask, 0.601 g (3.3 mmol) of acenaphthanedione, 0.284 g (3.3 mol) of 2,3-butanedione, 2.199 g (6.0 mmol) of 2,2-di(4-amino-3,5-diisopropyl phenyl) methane, and 50 ml ethanol were added, stirred and dissolved. Then, 1.0 ml of formic acid was added and the mixture was refluxed for 24 hours. After cooling, 0.283 g (1.6mmol) of 2,6-diisopropyl aniline was added, and the mixture was heated and refluxed for 24 hours. The rest of the procedure was the same as in Example 1. 2.88g of oligomer of α -diimine (yield 94.1%) was obtained.

Example 18

To a dried 150 ml reaction flask, 0.219 g (1.2 mmol) of phenanthrenedione, 0.465 g (5.4 mmol) of 2,3-butanedione, 2.199 g (6.0 mmol) of 2,2-di(4-amino-3,5-diisopropylphenyl)methane, and 50 ml of ethanol were added, stirred and dissolved. Then, 1.0 ml of formic acid was added dropwise and the mixture was refluxed for 24 hours. After cooling, 0.283 g (1.6 mmol) of 2,6-diisopropyl aniline was added and the mixture was heated and refluxed for 24 hours. The rest of the procedure was the same as in Example 1. 2.70 g of oligomer of α -diimine (yield 93.4%) was obtained.

Example 19

Under argon atmosphere, to a dried 100 ml Schlenk flask, 0.437 g (2.0 mmol) of NiBr_2 , 10 ml anhydrous CH_2Cl_2 , and 0.19 g of glycol dimethyl ether were added. The mixture was stirred for 15 minutes and then 0.998 g of α -diimine dimer prepared in Example 1 and 10 ml anhydrous CH_2Cl_2 were added, and the mixture was refluxed for 24 hours. After cooling, the mixture was poured into 60 ml of ethanol/petroleum ether mixture and filtered. The filter cake was washed 3 times with a little ether and vacuum dried at 60°C for 24 hours. 1.200 g (yield 83.6%) of dimer of α -diimino nickel(II)

bromide was obtained.

Example 20

The process of Example 19 was carried out, except that 1.055 g of trimer of α -diimine prepared in Example 2 was used in place of the dimer of α -diimine prepared in Example 1. 1.253 g (yield 84%) of trimer of α -diimino nickel(II) bromide was obtained.

Example 21

The process of Example 19 was carried out, except that 1.151 g of oligomer of α -diimine prepared in Example 3 was used in place of the dimer of α -diimine prepared in Example 1. 1.296 g (yield 81.6%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 22

The process of Example 19 was carried out, except that 0.976g of oligomer of α -diimine prepared in Example 4 was used in place of the dimer of α -diimine prepared in Example 1. 1.19 g (yield 84.2%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 23

The process of Example 19 was carried out, except that 1.139 g of oligomer of α -diimine prepared in Example 5 was used in place of the dimer of α -diimine prepared in Example 1. 1.344 g (yield 85.3%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 24

The process of Example 19 was carried out, except that 1.213 g of oligomer of α -diimine prepared in Example 6 was used in place of the dimer of α -diimine prepared in Example 1. 1.439 g (yield 87.2%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 25

Under argon atmosphere, to a dried 100 ml Schlenk flask, 0.259 g (2.0 mmol) of NiCl_2 , 10 ml anhydrous CH_2Cl_2 and 0.19 g of glycol dimethyl ether were added. The mixture was stirred for 15 minutes, then 1.213 g of α -diimine oligomer prepared in Example 7 and 10 ml of anhydrous CH_2Cl_2 were added, and thereafter, the mixture was refluxed for 24 hours. The rest of the procedure was the same as in Example 19. 1.257 g (yield 85.4) of oligomer of α -diimino nickel(II) chloride was obtained.

Example 26

The process of Example 19 was carried out, except that 1.213 g of oligomer of α -diimine prepared in Example 8 was used in place of the dimer of α -diimine prepared in Example 1. 1.481 g (yield 89.7%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 27

The process of Example 19 was carried out, except that 0.981 g of oligomer of α -diimine prepared in Example 9 was used in place of the dimer of α -diimine prepared in Example 1. 1.191 g (yield 84.0%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 28

The process of Example 19 was carried out, except that 0.873 g of the product prepared in Example 10 was used in place of the dimer of α -diimine prepared in Example 1. 1.081 g (yield 82.5%) of dimer of α -diimino nickel(II) bromide was obtained.

Example 29

The process of Example 19 was carried out, except that 1.070 g of dimer of α -diimine prepared in Example 11 was used in place of the dimer of α -diimine prepared in Example 1. 1.252 g (yield 83.1%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 30

The process of Example 19 was carried out, except that 0.831 g of oligomer of α -diimine prepared in Example 12 was used in place of the dimer of α -diimine prepared in Example 1. 1.047 g (yield 82.6%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 31

The process of Example 19 was carried out, except that 0.831 g of oligomer of α -diimine prepared in Example 13 was used in place of the dimer of α -diimine prepared in Example 1. 1.066 g (yield 84.1%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 32

The process of Example 19 was carried out, except that 0.832g of oligomer of α -diimine prepared in Example 14 was used instead of the dimer of α -diimine prepared in Example 1. 1.091 g (yield 86.0%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 33

The process of Example 19 was carried out, except that 0.860g of oligomer of α -diimine prepared in Example 15 was used in place of the dimer of α -diimine prepared in Example 1. 1.148 g (yield 88.5%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 34

The process of Example 19 was carried out, except that 1.345g of oligomer of α -diimine prepared in Example 16 was used in place of the dimer of α -diimine prepared in Example 1. 1.622 g (yield 91.0%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 35

The process of Example 19 was carried out, except that 1.020 g of oligomer of α -diimine prepared in Example 17 was used in place of the dimer of α -diimine prepared in Example 1. 1.370 g (yield 94.1%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 36

The process of Example 19 was carried out, except that 0.963 g of oligomer of α -diimine prepared in Example 18 was used in place of the dimer of α -diimine prepared in Example 1. 1.289 g (yield 92.1%) of oligomer of α -diimino nickel(II) bromide was obtained.

Example 37

Under ethylene atmosphere, to a dried 250 ml flask, 14.4 mg ($20 \mu\text{mol Ni}$) of dimer of α -diimino nickel bromide prepared in Example 19 and 50 ml of absolute toluene were added. The dimer was dissolved with stirring and the mixture was heated to 35°C . 8 ml of 1M MAO was added, and the polymerization reaction was allowed to proceed under normal pressure for 30 minutes. The mixture was poured into 200 ml of 1% ethanol solution of HCl/ water (2:1). The toluene layer was separated, and toluene was evaporated by reduced pressure. 0.58 g of a rubbery polymer was obtained. The catalytic efficiency is $5.8 \times 10^4 \text{ g PE/mol Ni} \cdot \text{h}$.

Example 38

The process of Example 37 was carried out, except that 25 mg ($20 \mu\text{mol Ni}$) of trimer of α -diimine Ni(II) bromide prepared in Example 20 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.54 g of a rubbery polymer was obtained. The catalytic efficiency is $5.4 \times 10^4 \text{ g PE/mol Ni} \cdot \text{h}$.

Example 39

The process of Example 37 was carried out, except that 23.8 mg ($30 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 21 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.79 g of a rubbery

polymer was obtained. The catalytic efficiency is 5.3×10^4 g PE/mol Ni · h.

Example 40

The process of Example 37 was carried out, except that 18.4 mg ($26 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 22 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.64 g of a rubbery polymer was obtained. The catalytic efficiency is 4.8×10^4 g PE/mol Ni · h.

Example 41

The process of Example 37 was carried out, except that 16.6 mg ($21 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 23 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.56 g of a rubbery polymer was obtained. The catalytic efficiency is 5.3×10^4 g PE/mol Ni · h.

Example 42

The process of Example 37 was carried out, except that 16.5 mg ($20 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 24 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.51 g of a rubbery polymer was obtained. The catalytic efficiency is 5.1×10^4 g PE/mol Ni · h.

Example 43

The process of Example 37 was carried out, except that 19 mg ($23 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel chloride prepared in Example 25 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.53 g of a rubbery polymer was obtained. The catalytic efficiency is 4.6×10^4 g PE/mol Ni · h.

Example 44

The process of Example 37 was carried out, except that 19.8 mg ($24 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 26 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.59 g of a rubbery polymer was obtained. The catalytic efficiency is 4.9×10^4 g PE/mol Ni · h.

Example 45

The process of Example 37 was carried out, except that 14.2 mg ($20 \mu\text{mol Ni}$) of the dimer of α -diimino nickel bromide prepared in Example 27 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.42 g of a rubbery polymer was obtained. The catalytic efficiency is $4.2 \times 10^4 \text{ g PE/mol Ni} \cdot \text{h}$.

Example 46

The process of Example 37 was carried out, except that 16.8 mg ($25.8 \mu\text{mol Ni}$) of the dimer of α -diimino nickel bromide prepared in Example 28 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.82 g of a rubbery polymer was obtained. The catalytic efficiency is $6.4 \times 10^4 \text{ g PE/mol Ni} \cdot \text{h}$.

Example 47

The process of Example 37 was carried out, except that 15.1 mg ($20 \mu\text{mol Ni}$) of the dimer of α -diimino nickel bromide prepared in Example 29 was used in place of the dimer of α -diimino nickel bromide prepared in Example 38. 0.38 g of a rubbery polymer was obtained. The catalytic efficiency is $3.8 \times 10^4 \text{ g PE/mol Ni} \cdot \text{h}$.

Example 48

Under ethylene atmosphere, to a dried 250 ml reaction flask, 15 mg ($23.6 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 30 and 50 ml of absolute toluene were added, and the mixture was stirred and dissolved. The solution was heated to 35°C . Then, 9 ml of 1M MAO was added, and the polymerization reaction was allowed to proceed under normal pressure for 60 minutes. Then, the mixture was poured into 200 ml of 1% ethanol solution of HCl, filtered and washed 3 times with ethanol and finally vacuum dried at room temperature. 0.35 g of a polymer was obtained. The catalytic efficiency is $1.5 \times 10^4 \text{ g PE/mol Ni} \cdot \text{h}$.

Example 49

The process of Example 48 was carried out, except that 18 mg ($28.4 \mu\text{mol Ni}$) of

the oligomer of α -diimino nickel bromide prepared in Example 31 was used in place of the oligomer of α -diimino nickel bromide prepared in Example 30. 0.40 g of a polymer was obtained. The catalytic efficiency is 1.4×10^4 g PE/mol Ni · h

Example 50

The process of Example 48 was carried out, except that 20 mg ($31.5 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 32 was used in place of the oligomer of α -diimino nickel bromide prepared in Example 30. 0.51 g of a polymer was obtained. The catalytic efficiency is 1.6×10^4 g PE/mol Ni · h

Example 51

The process of Example 48 was carried out, except that 21 mg ($32.5 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 33 was used in place of the oligomer of α -diimino nickel bromide prepared in Example 30. 0.48 g of a polymer was obtained. The catalytic efficiency is 1.5×10^4 g PE/mol Ni · h

Example 52

The process of Example 37 was carried out, except that 20.3 mg ($22.9 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 34 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.62 g of a rubbery polymer was obtained. The catalytic efficiency is 5.4×10^4 g PE/mol Ni · h

Example 53

The process of Example 37 was carried out, except that 20 mg ($22.5 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 35 was used in place of the dimer of α -diimino nickel bromide prepared in Example 19. 0.44 g of a rubbery polymer was obtained. The catalytic efficiency is 3.3×10^4 g PE/mol Ni · h

Example 54

The process of Example 37 was carried out, except that 15 mg ($21.5 \mu\text{mol Ni}$) of the oligomer of α -diimino nickel bromide prepared in Example 36 was used in place of

the dimer of α -diimino nickel bromide prepared in Example 19. 0.44 g of a rubbery polymer was obtained. The catalytic efficiency is 2.1×10^4 g PE/mol Ni · h

Example 55

Under ethylene atmosphere, to a dried 1 liter autoclave, 75 mg (0.1 mmol Ni) of the trimer of α -diimino nickel bromide prepared in Example 20 and 300 ml absolute toluene were added. The trimer was dissolved with stirring and the mixture was heated to 35°C. 50 ml of 1M MAO was added, and the pressure was raised. The polymerization reaction was allowed to proceed under 1.0 MPa for 30 minutes. The polymerization reaction was terminated with 1% ethanol solution of HCl. The reaction mixture was filtered and vacuum dried at 60°C for 24 hours. 104 g of a polymer was obtained. The catalytic efficiency is 2.1×10^6 g PE/mol Ni · h.